(12) UK Patent Application (19) GB (11) 2 074 745 A

(21) Application No 8111187
(22) Date of filing
9 Apr 1981
(30) Priority data
(31) 55/045666
55/063050
55/065692
(32) 9 Apr 1980
13 May 1980
16 May 1980
(33) Japan (JP)
(43) Application published
4 Nov 1981
(51) INT CL³ G03G 9/08
(52) Domestic classification
G2C 1102 1104 1106
1107 1108 1109 1113
1116 1118 1121 1122
1126 1128 1129 1130
1131 1137 1138 1148
1149 1171 1172 1173
C17Q2
(56) Documents cited
GB 2046930A
GB 1563209
GB 1563208
(58) Field of search
G2C

(71) Applicant
Ricoh Company Ltd
3–6 1-chome
Nakamagome
Ohta-ku
Tokyo
Japan
(72) Inventors
Nobuo Mochizuki
Toshiyasu Kawabata
Toshio Kaneko
Hachiro Tosaka
Masaki Takatsugi
(74) Agents
Marks & Clerk
57–60 Lincoln's Inn
Fields
London WC2A 3LS

(54) Developer for developing latent electostatic images

(57) A developer for developing latent electrostatic images and particularly for use in copying apparatus employing the magnetic brush principle comprises a mixture of (a) magnetic toner particles having a high electrical resistivity (e.g. having a volume resistivity of 10^{12} ohm.cm or more) and (b) electrically conductive magnetic particles (e.g. having a volume resistivity of 10^{9} ohm.cm or less) having an average particle size less than that of the magnetic toner particles, suitably from one-fifth to four-fifths that of the magnetic toner particles. The developer may also contain finely powdered materials which are such as can be triboelectrically charged to that of a latent electrostatic image to be developed when brought into contact with a development sleeve of a magnet brush type copying apparatus. The electrically conductive material may be formed of coagulated sub-particles. The developer suitably contains from 98 to 60% by weight of the magnetic toner particles and from 2 to 4% by weight of the electrically conductive magnetic particles.

GB 2 074 745 A

FIG. 1(a)

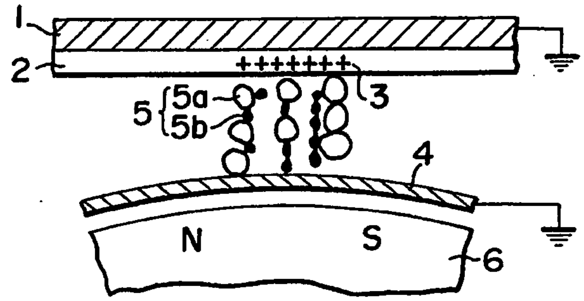


FIG. 1(b)

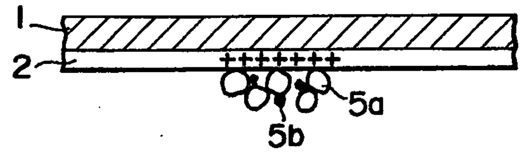


FIG. 3

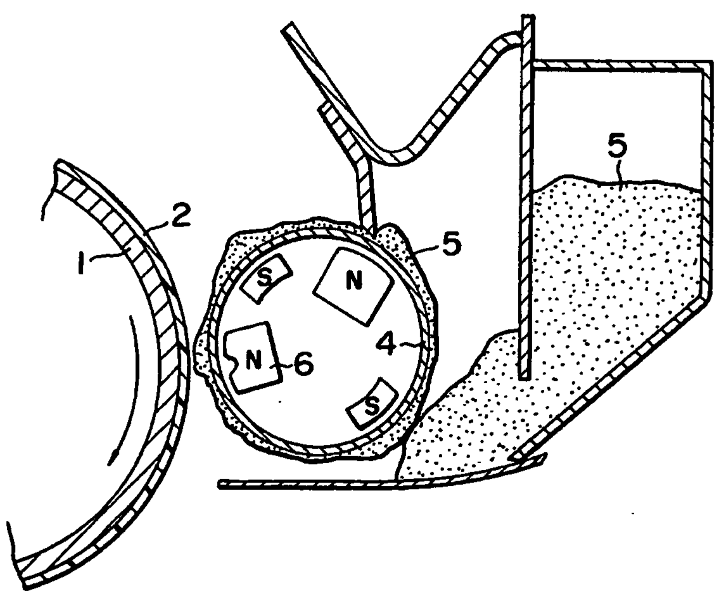
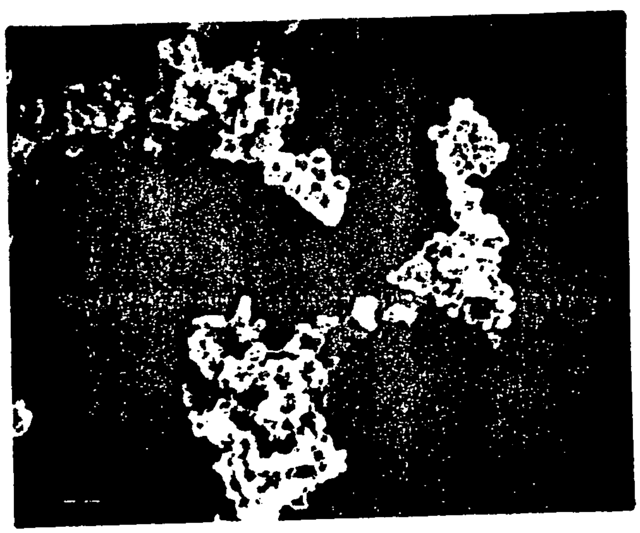


FIG. 2



1 μm

SPECIFICATION

Developer for developing latent electrostatic images

The present invention relates to a developer for developing latent electrostatic images and a development process using the said developer.

There is known a development method for developing latent electrostatic images using a so-called "one-component" magnetic toner which consists only of an electrically conductive magnetic toner. In this development method, the so-called "magnetic brush" method, the electrically conductive magnetic toner is attracted to and held on the surface of an electrically conductive non-magnetic development sleeve provided with internal magnets, through the magnetic force of the magnets. The development sleeve and the magnets are moved relative to each other to carry the magnetic toner onto a latent electrostatic image formed on a latent image bearing member comprising a photoconductive layer supported on an electrically conductive support. When the magnetic toner is carried onto the latent electrostatic image, electronically conductive paths are formed between the magnetic toner and the development sleeve, and the magnetic toner becomes electrically charged to a polarity opposite to that of the latent electrostatic image, so that the latent electrostatic image is developed by the magnetic toner. The electrically conductive magnetic toner employed in this development method is more electrically conductive at portions near the surface of the toner particles than in the central portions thereof, as is disclosed in United States Patent No. 3,639,245. Such electrically conductive magnetic toners, however, have the disadvantage that it is difficult to effect electrostatic transfer of the toner images developed by the electrically conductive magnetic toner to other recording materials.

In order to overcome this disadvantage, a method using a magnetic toner with increased electrical resistivity has been proposed. However, this method leads to a reduction in the development performance of the magnetic toner.

According to one embodiment of the invention there is provided a developer for developing latent electrostatic images, which developer has good development performance and image transfer performance and comprises (1) a magnetic toner with high electric resistivity and in which magnetic fine particles are dispersed, and (2) electrically conductive magnetic particles whose average particle size is smaller than the particle size of the magnetic toner.

In accordance with a further embodiment of the invention there is provided a developer of the type described also containing a fine powdered material, which fine powdered material becomes charged triboelectrically to the same polarity as that of the latent electrostatic image to be developed when it is brought into contact with a development sleeve, because of the triboelectricelectric-charging-series relationship between the powder-like material and the material of the development sleeve. By the addition of the powder-like material, the developer is particularly improved so as to eliminate toner desposition on the non-image areas of a latent electrostatic image bearing member.

In accordance with a yet further embodiment of the invention there is provided a developer of the first mentioned type, in which each of the electrically conductive magnetic particles comprises a number of sub-particles which are made in a manner such that the sub-particles freely coagulate. The electrically conductive magnetic particles thus formed facilitate the formation of electronically conductive paths between the magnetic toner and the development sleeve. Moreover, when image fixing is performed by a roller, the image fixing roller is prevented from being scratched or damaged by the magnetic toner since the electrically conductive magnetic particles easily collapse during the image fixing procedure and act as cushions for the magnetic toner.

In the following description reference will be made to the accompanying drawings in which:—

Figure 1 (a) and Figures 1(b) are diagrammatic illustrations to explain the development mechanism using a developer according to the present invention;

Figure 2 is a microphotograph of the coagulated electrically conductive magnetic particles which are employed in one embodiment of a developer according to the present invention; and

Figure 3 is a diagrammatic drawing of an example of a development apparatus in which a developer according to the present invention is employed.

The development mechanism using a developer according to the present invention is shown diagrammatically in Figs. 1(a) and 1(b) of the accompanying drawings.

Fig. 1 (a) shows the development mechanism in the case of a latent electrostatic image-bearing layer 2 which is supported on an electrically conductive support material 1. A layer of developer 5, according to the present invention and which comprises magnetic toner particles with high electric resistivity, 5a, and electrically conductive magnetic particles 5b, is held on a development sleeve 4. The developer 5 is carried onto a latent electrostatic image on layer 2 by the sleeve 5 and a magnet 6 enclosed in the sleeve 5, which are moved relative to each other. At

this moment, electric charges with a polarity opposite to that of the latent electrostatic image are induced by the sleeve 4 in the electrically conductive magnetic particles 5b. Part of the thus generated electric charge is accumulated in the magnetic toner particles 5a which are located near the latent electrostatic image. As a result, the magnetic toner particles 5a and the electrically conductive magnetic particles 5b are attracted to the latent electrostatic image, so that the latent electrostatic image is developed. Fig. 1 (b) shows the state in which the latent electrostatic image has been developed. As can be seen from Fig. 1(b), both the magnetic toner particles 5a and the electrically conductive magnetic particles 5b contribute to the development. However, per unit weight of the magnet 6, the magnetic toner particles 5a are more attracted to the latent electrostatic image than the electrically conductive magnetic particles 5b, since more attracting force is applied to the magnetic toner particles 5a than to the electrically conductive magnetic particles 5b. In a subsequent image transfer process, the developed image as shown in Fig. 1(b) is superimposed upon a recording material, such as plain paper, and is then transferred thereto by an electrostatic image transfer means, for example by means of a corona charging apparatus. In this image transfer process, the magnetic toner particles 5a with high electric resistivity are transferred to the recording material to a greater degree than are the electrically conductive magnetic particles 5b. Some of the electrically conductive magnetic particles 5b, attracted weakly to the magnetic toner particles 5a, are also transferred to the recording material together with the magnetic toner particles 5a.

In order to accomplish the above-mentioned development process, one of the most important requirements for the developer according to the present invention is that the average particle size of the electrically conductive magnetic particles 5b be smaller than that of the magnetic toner particles 5a. By the term "average particle size" as used herein we mean the volume mean diameter of the particles.

If the average particle size of the electrically conductive magnetic particles 5b is greater than that of the magnetic toner particles 5a, the electrically conductive magnetic particles 5b are covered with the magnetic toner particles 5a. As the size of the electrically conductive magnetic particles 5b increases, the magnetic attracting force applied to the magnetic particles 5b by the magnet 6 increases. As a result, the magnetic particles 5b bearing the magnetic toner particles 5a tend to be removed from the latent electrostatic image area, producing halos in the latent electrostatic image areas. The same phenomenon occurs during the image transfer process, since the electrically conductive magnetic particles 5b are harder to transfer electrostatically than are the magnetic toner particles 5a.

However it, it is not desirable that the average size of the magnetic particles 5b be extremely small in comparison with that of the magnetic toner particles 5a. If the magnetic particles 5b are very small in comparison to the magnetic toner particles 5a, the magnetic particles 5b are firmly attracted to the surfaces of the magnetic toner particles 5a by Van der Waals forces. As a result, each toner particle comes to have a similar construction to that of the conventional magnetic toner particle, with its surface layer more electrically conductive than the central portion thereof. Consequently, the image transfer performance of the magnetic toner particles 5a is significantly degraded. For this reason, it is preferable that the particle size of the electrically conductive magnetic particles 5b be from one-fifth to four-fifths the particle size of the magnetic toner particles 5a, and more preferably from three-tenths to two-thirds of the particle size of the magnetic toner particles 5a.

The electric conductivity of the electrically conductive magnetic particles 5b should be 10^9 ohm.cm or less in terms of volume resistivity, and the resistivity of the magnetic toner particles 5 should be 10^{12} ohm.cm or more in terms of volume resistivity.

The volume resistivity of the magnetic toner particles 5a or of the electrically conductive magnetic particles 5b is measured as follows. One ml of a sample of the magnetic toner particles 5 a or of the electrically conductive magnetic particles 5b is placed in a cylindrical container, the bottom of which is made of an electrode disc with an inner diameter of 20 mm and the side wall of which is made of an electrically insulating material. An electrode disc which is less than 20 mm in diameter and weighs 100 g is then placed over the sample. The sample is allowed to stand in at state for one hour and a D.C. potential of 100 volts is applied across the two electrodes. The electric current which flows through the sample is measured after the application of the above-mentioned voltage for 1 minute. From the thus measured electric current, the volume resistivity of the sample is calculated.

The electrically conductive magnetic particles 5b for use in the present invention may be formed of any magnetizable material, for example metals such as Fe, Ni, Co and Mn, and oxides and alloys thereof. It is preferable that the electrically conductive magnetic particles 5b consist only of one or more of the magnetizable materials. Such electrically conductive magnetic particles, however, can also be prepared by dispersing a magnetic powder with an average particle size of 1 micron or less in a resin, if necessary with the addition of an electroconductive agent, and then forming the dispersion into particles of the desired

size.

As magnetic toner particles with high resistivity, 5a, for use in the present invention, there can be used conventional magnetic toner particles which essentially consist of polymeric materials and magnetic powder materials, if necessary with the addition thereto of a colouring agent and a material for improving the flowability of the magnetic toner particles 5a. Suitable polymeric materials include, for example, polystyrene, acrylic resins, vinyl resins, epoxy resins, polyester resins, phenolic resins, polyurethane resins, natural resins and cellulose. As the magnetic powder materials for the magnetic toner particles, magnetizable materials, such as metals, for example Fe, Ni, Co and Mn, and oxides and alloys of such metals, with an average particle size of 1 micron or less, can be employed. As the colouring agent there can be employed pigments or dyes, such as Carbon Black, Aniline Black, Crystal Violet, Rhodamine B, Malachite Green, Nigrosine, copperphthalocyanine and azo dyes. When necessary, waxes, fatty acids, metallic salts of fatty acid, powdered silica or powered zinc oxide can be added to the colouring agent.

It has been found that is is preferable that the magnetic toner have a tendency to be triboelectrically charged to a polarity opposite to that of the charges applied to an image transfer sheet in the electrostatic image transfer process, in order to attain high image transfer efficiency. In order to cause the magnetic toner to have such a tendency, it is preferred to add to the magnetic toner so-called "charge control agents" which are high polar materials such as Nigrosine, monozao dyes, zinc hexadecylsuccinate, alkyl esters or alkyl amides of naphthoic acid, nitrohumic acid, N,N'-tetramethyldiaminobenzophenone, N,N'-tetramethylbenzidine, triazine, and metal complexes of salicylic acid.

The developer according to the present invention is prepared by mixing the electrically conductive magnetic particles with the magnetic toner particles of high electrical resistivity. In such mixtures, the electrically conductive magnetic particles suitably form from 2 to 40% by weight, preferably from 10 to 30% by weight, of the mixture and the magnetic toner particles suitably form from 98 to 60% by weight, preferably from 90 to 70% by weight of the mixture. Such a developer may also contain conventional flow-improvement agents, such as silica, hard resinous powders, zinc oxide, higher fatty acids, metallic salts of higher fatty acid, silicone oils and fluorine-containing oils.

In the simplest embodiment, the developers according to the invention consist of a mixture of magnetic toner particles and electrically conductive magnetic particles, possibly in admixture with flow improvement agents. Such developers have the advantage over conventional two-component developers employed in a magnetic brush development method, in that triboelectric charging using magnetic carriers is unnecessary for the developers according to the present invention, in contrast to the conventional two-component developer. Because of this advantage, the development apparatus for this developer can be made compact in size. Another advantage of the present developers is that they are stable to changes in ambient temperature.

However, the development initiation potential required for such developers may be slightly low and, therefore, toner deposition on the background of the developed images may take place. In order to overcome this disadvantage a fine powdered material may be added to the developers which powdered material is triboelectrically charged to the same polarity as that of the latent electrostatic image to be developed, when it is brought into contact with a development sleeve, because of the triboelectric-charging-series relationship between the powder-like material and the material of the development sleeve.

Examples of powdered materials for increasing the development initiation potential of the developer include zinc oxide, titanium oxide, silicon oxide, magneisum oxide, aluminium oxide, calcium carbonate, magnesium carbonate, barium carbonate, barium sulphate, calcium sulphate, aluminium hydroxide, magnesium hydroxide, calcium silicate, magnesium silicate, clay, white carbon, alumina white and talc.

The position of each of these materials and that of the material of the development sleeve, in terms of the triboelectric charging series, can be easily confirmed by rubbing each of the materials against the development sleeve. Further, their relative positions in terms of the triboelectric charging series are also reported in various works of reference. Based on the information contained in the references, the desired materials can be selected from the above-mentioned materials. For instance, when the development sleeve is made of aluminium and a latent electrostatic image with a positive polarity formed on a selenium photoconductor is to be developed, aluminium powder is suitable for use. When a latent electrostatic image with a negative polarity formed on a zinc oxide photoconductor is to be developed, silica powder and titanium oxide powder are suitable. The powders can be used without any treatment, but when a particular triboelectric characteristic is desired, they may be treated with a surface active agent or a charge control agent. When they are treated with such agents, the range of choice of materials can be broadened.

It is preferred that the average particle size of the powdered material be 0.5 micron or less and the amount of the material added to the developer be from 0.1 to 5.0% by

weight, based on the weight of the magnetic toner. If the amount of the powdered material added to the developer is less than 0.1% by weight, based on the weight of the magnetic toner, it is difficult to obtain an increase in the development initiation potential of the developer; while if the amount of the powdered material is greater than 5.0% by weight on the same basis, the image density may be decreased.

The powdered material may be incorporated in the developer by first mixing it with the magnetic toner or the electrically conductive magnetic particles and then adding the resultant mixture to the electrically conductive magnetic particles or to the magnetic toner, as the case may be. Alternatively, the three components can be mixed together at the same time. It is, however, preferred to first mix the magnetic toner and the powdered material and then mix the resultant mixture with the electrically conductive magnetic particles.

By adding a powdered material which is triboelectrically charged to the same polarity as that of the latent electrostatic image, because of the triboelectric-charging-series relationship between the powder-like material and the material of the development sleeve, the development initiation potential of the developer can be increased and, accordingly, the deposition of the magnetic toner on the background of the developed image can be avoided.

In order to further improve the development performance of the developer of the invention, each of the electrically conductive magnetic particles may be made by coagulating a number of sub-particles. By such coagulation of the sub-particles, the formation of the electrically conductive paths between the magnetic toner and the development sleeve is facilitated, so that the development performance of the developer may be significantly improved. Moreover, by such coagulation, the electrically conductive magnetic particles may be such as to easily collapse under pressure applied thereto during the image fixing process, so that the image fixing rollers of the development apparatus are not scratched or damaged by the magnetic toner mixed with the electrically conductive magnetic particles.

Referring to Fig. 2, there is shown a mocrophotograph of electrically conductive magnetic particles of such a coagulated type.

The coagulated electrically conductive magnetic particles can be prepared as follows.

Very small electrically conductive magnetic particles, which serve as the aforementioned sub-particles, are washed with water and then thoroughly dried with stirring in a drying apparatus. Alternatively, a fluidized bed of the very small electrically conductive magnetic sub-particles is formed and the fluidized bed is sprayed with an organic polymeric material so as to bond the sub-particles with the sprayed organic materials. As mentioned previously, as the electrically conductive magnetic materials, there may be employed magnetizable materials, such as metals including Fe, Ni, Co and Mn, and oxides and alloys of such metals. For the sub-particles of the coagulated electrically conductive magnetic particles, metal particles having an average particle size of from about 0.01 to 0.5 microns are suitable for use.

The developers of the invention are, as noted above, suitable for use as magnetic brush type copying apparatus for example as described in British Patent Specification No. 1216915 or as diagrammatically illustrated in Fig. 3 of the accompanying drawings. This latter apparatus comprises a latent electrostatic image bearing member comprising a layer of a photoconductive material 2 supported on an electrically conductive drum 1 which is provided with means (not shown) for rotating it in the direction indicated by the arrow. Developer 5, in accordance with the invention, is brought from supply hopper 7 into contact with latent, image-bearing layer 2 by means of sleeve 4 provided with internal magnets 6, sleeve 4 being rotated in a conterclockwise direction (with magnets 6 remaining stationary) to effect such transfer.

In order that the invention may be well understood the following examples are given by way of illustration only. In the examples all parts and percentages are by weight unless otherwise stated.

EXAMPLE 1

(a) A mixture of 100 parts of Piccolastic D–125 (polystyrene manufactured by Esso Standard Oil Co. Ltd.), 10 parts of carbon black, 2 parts of 2–hydroxy–3–naphthoic acid isoamyl ester and 40 parts of magnetite having an average particle size of 0.1 micron was kneaded with heating by means of heated rollers. After cooling, the mixture was ground to a powder and the powder was classified to give a magnetic toner having an average particle size of 20 microns and an electrical resistivity of 4×10^{12} ohm.cm.

(b) 75 Parts of the magnetic toner prepared in (a) above were mixed were 25 parts of Fe_3O_4 particles having an average particle size of 13 microns and an electrical restivity of 3×10^7 ohm.cm to give a developer according to the present invention (developer No.1).

(c) A latent electrostatic image with a positive polarity was formed on a selenium photoconductor by a conventional electrophotographic procedure. The latent electrostatic image was then developed with developer No. 1 using development apparatus as shown in Fig. 3. The developed image was transferred to plain paper by the application of positive corona charges thereto and was then fixed onto the plain paper by the application of heat. As a result, a clear copy image without any halos was obtained.

EXAMPLE 2

(a) A mixture of 100 parts of Pliolite (Polyvinyl toluene manufactured by Goodyear Co. Ltd.), 1 part of carbon black, 2 parts of sodium nitrohuminate and 30 parts by weight of magnetite having an average particle size of 0.1 micron, was kneaded, powdered, cooled and classified as described in Example 1(a) to give a magnetic toner having an average particle size of 15 microns and an electrical resistivity of 8×10^{13} ohm.cm.

(b) 80 Parts of the magnetic toner prepared in (a) above were mixed with 20 parts of iron powder having an average particle size of 6 microns and an electrical resistivity of 2×10^{5} ohm.cm, to give developer No. 2 according to the invention.

(c) Developer No 2 was used to form a fixed image on plain paper following the procedure described in Example 1(c). A clear copy image without any halos was obtained.

EXAMPLE 3

(a) A mixture of 100 parts of a styrene-methyl methacrylate copolymer, 2 parts of Nigrosine and 100 parts of magnetite having an average particle size of 0.1 micron, was kneaded, cooled, powdered, and classified as described in Example 1 (a) to give a magnetic toner having an average particle size of 12 microns and an electrical resistivity of 7×10^{14} ohm.cm.

(b) 70 Parts of the magnetic toner prepared in (a) above were mixed with 30 parts of ferrite particles having an average particle size of 6 microns and an electrical resistivity of 6×10^{8} ohm.cm to give developer No. 3 according to the invention.

(c) A latent electrostatic image with a negative polarity was formed on a layered organic photoconductor by a conventional electrophotographic procedure. This layered organic photoconductor comprised an aluminium-coated polyester film, a charge generating layer having a thickness of 2 microns and consisting of Chlorodiane Blue formed on the electrically conductive aluminium-coated polyester film, and a charge transport layer having a thickness of 20 microns and comprising 50% of 1-phenyl-3-[*p*-diethylaminostyryl]-5-[*p*-diethylaminophenyl]- pyrazoline and 50% of a polycarbonate resin, which charge transporting layer was formed on the charge generating layer. The latent electro-static image was then developed with developer No.3 using development apparatus as shown in Fig. 3. The developed image was transferred to plain paper by the application of negative corona charges thereto and was then fixed to the plain paper by application of heat. As a result, a clear copy image without any halos was obtained.

EXAMPLE 4

(a) A mixture of 10 parts of Piccolastic D-125, 30 parts of magnetite having an average particle size of 0.1 micron and 0.2 parts by weight of carbon black, was kneaded, cooled, powdered and classified following the procedure described in Example 1(a) to give electrically conductive magnetic particles having an average particle size of 9 microns and an electrical restivity of 4×10^{7} ohm.cm.

(b) 25 Parts of the electrically conductive magnetic particles produced in (a) above were mixed with 75 parts of the magnetic toner prepared in Example 1(a) to give developer No. 4 according to the invention.

(c) Developer No. 4 was used to form a fixed image on plain paper following the procedure of Example 1(c). A clear copy image without any halos was obtained.

EXAMPLE 5

75 Parts of the magnetic toner prepared in Example 1(a) were mixed with 1.5 parts of alumina white having an average particle size of 0.1 micron. To this mixture, 25 parts of Fe_3O_4 particles having an average particle size of 13 microns and an electrical resistivity of 3×10^{7} ohm.cm were added and the whole was mixed to give developer No. 5.

A latent electrostatic image with a positive polarity was formed on a selenium photoconductor by a conventional electrophotographic procedure. The latent electrostatic image was then developed with developer No. 5 using development apparatus as shown in Fig. 3. (The development sleeve in the development apparatus was made of aluminum). The developed image was transferred to plain paper by the application of positive corona charges thereto and was then fixed to the plain paper by the application of heat. As a result, a clear copy image without any halos was obtained.

The copy image obtained using developer No. 5 and that obtained using developer No. 1 were compared with each other. Developer No.1 is a developer which does not contain aluminium white but whose other components are exactly the same as those of developer No. 5. The result was that both copy images were clear and free from halos, but that the copy image obtained using developer No.1 had slight toner deposition on the background, while the copy image obtained using developer No. 5 was completely free from such toner deposition.

In accordance with the same procedure as in Example 5, except that alumina white was replaced by silica powder having an average particle size of 0.1 microns, a modified developer (No. 5M) was prepared. A latent electrostatic image was developed using developer No. 5M and the developed image was transferred to plain paper. The result was that toner deposition on the background was conspicuous.

EXAMPLE 6

Silica powder having an average particle size of 0.1 microns was treated with a Nigrosine dye solution by immersing the powder in the Nigrosine dye solution and drying it after separating it from the dye solution.

80 Parts of the magnetic toner prepared as described in Example 2(a) were mixed with 4 parts of the treated silica powder. To this mixture were then added 20 parts of iron powder having an average particle size of 6 microns and an electrical resistivity of 2×10^5 ohm.cm. The mixture was then well mixed, to give developer No. 6 according to the invention.

Developer No. 6 was used to form a fixed image on plain paper following the procedure of Example 1(c). A clear copy image without any halos or any toner deposition on the background was obtained.

EXAMPLE 7

70 Parts of the magnetic toner prepared as described in Example 3(a) were mixed 1.4 parts of titanium oxide powder having an average particle size of 0.5 micron. To the mixture were added 30 parts of ferrite particles having an average particle size of 6 microns and an electrical resistivity of 6×10^8 ohm.cm. The mixture was well mixed to give developer No. 7.

Developer No. 7 was used to form a fixed image on plain paper following the procedure described in Example 3(a). A clear copy image without any halos or any toner deposition on the background of the copy image was obtained.

The copy image obtained using Developer No. 7 and that obtained using Developer No. 3 were compared with each other. Developer No.3 is a developer which does not contain the titanium oxide powder, but whose other components are exactly the same as those of developer No. 7. The result was that both copy images were clear and free from halos, but the copy image obtained using developer No. 3 had slight toner deposition on the background, while the copy image obtained using developer No. 7 was completely free from such toner deposition.

EXAMPLE 8

75 Parts of the magnetic toner prepared as described in Example 1(a) and 1 part of silica powder having an average particle size of 0.1 micron and which had been treated with a Nigrosine dye as described in Example 6, were mixed together.

The resultant mixture was mixed with 25 parts of the electrically conductive magnetic particles prepared as described in Example 4(a), to give developer No. 8. according to the invention.

Developer No. 8 was used to form a fixed image on plain paper following the procedure described in Example 1 (a). A clear copy image without any halos or any toner deposition on the background was obtained.

EXAMPLE 9

500 g of 20% ammonia water were added to 1,500g of a 10% aqueous $FeSO_4.7H_2O$ solution. To the mixture was added dropwise 500 g of a 10% aqueous KNO_3 solution, while the mixture was boiled in an atmosphere shielded from air. Cubic fine crystals of Fe_3O_4 were separated. These crystals were extremely small in diameter and were used to constitute the sub-particles of the electrically conductive magnetic particles, as follows.

The crystals were washed with water and were then thoroughly dried with stirring in a drying apparatus, whereby the fine sub-particles of Fe_3O_4 coagulated into the shape of bunches of grapes, the electrically conductive magnetic particles. These particles were classified, to give electrically conductive magnetic particles having an average particle size of 5 microns and an electrical resistivity of 3×10^6 ohm.cm.

90 Parts of the magnetic toner prepared as described in Example 1(a) and 10 parts of the coagulated electrically conductive magnetic particles were mixed to give developer No. 9 according to the invention.

A latent electrostatic image with a positive polarity was formed on a selenium photoconductor by a conventional electrophotographic procedure. The latent electrostatic image was then developed with developer No 9 using development apparatus as shown in Fig. 3. The developed image was transferred to plain paper by the application of positive corona charges and was then fixed to the plain paper by the application of heat by a silicone rubber roller. As a result, a clear copy image with high image density and free from any halos was obtained.

The above-mentioned copying process was repeated 1,000 times. Hardly any scratches at all were observed on the surface of the silicone rubber roller.

This copying process was repeated using a developer containing uncoagulated electrically conductive magnetic particles, instead of the coagulated electrically conductive magnetic particles, but whose other components were exactly the same as those of Developer No. 9. The copying process was repeated 1,000 times and scratches were conspicuous all over the surface of the silicone rubber roller.

EXAMPLE 10

70 Parts of the magnetic toner prepared as described in Example 3(a) were mixed with 1.4 parts by weight of titanium oxide powder having an average particle size of 0.5 micron. To the mixture were added 30 parts by weight of the coagulated electrically conduc-

tive magnetic particles prepared as described in Example 9, to give developer No. 10.

Developer No. 10 was used to form a fixed image on plain paper following the procedure described in Example 9. A clear copy image with high image density and free from any halos or any toner deposition on the background of the copy image was obtained.

The copying process was repeated 1,000 times. Hardly any scratches were observed on the surface of the silicone rubber roller.

CLAIMS

1. A developer for developing latent electrostatic images comprising:
(a) a magnetic toner having a high electrical resistivity and having fine magnetic particles dispersed therein; and
(b) electrically conductive magnetic particles having an average particle size less than that of the magnetic toner.

2. A developer as claimed in claim 1, wherein the electrically conductive magnetic particles (b) are formed of Fe, Ni, Co and Mn or an oxide or alloy thereof.

3. A developer as claimed in claim 1 or claim 2, wherein the average particle size of the electrically conductive magnetic particles is from one-fifth to four-fifths that of the magnetic toner.

4. A developer as claimed in any one of the preceding claims wherein the magnetic toner has an average particle size of from 5 to 20 microns.

5. A developer as claimed in any one of the preceding claims wherein the mixture of the electrically conductive magnetic particles and the magnetic toner contains from 2 to 40% by weight of the electrically conductive magnetic particles and from 98 to 60% by weight of the magnetic toner.

6. A developer as claimed in any one of the preceding claims wherein each of the electrically conductive magnetic particles comprises a number of coagulated electrically conductive magnetic sub-particles.

7. A developer as claimed in claim 6, wherein said electrically conductive magnetic sub-particles are made of Fe, Ni, Co and Mn or oxides or alloys thereof.

8. A developer as claimed in claim 6 or claim 7, wherein the average particle size of the electrically conductive magnetic sub-particles is from 0.01 to 0.5 microns.

9. A developer as claimed in any one of claims 6–8 wherein the electrically conductive magnetic sub-particles are bonded together with an organic polymeric material.

10. A developer as claimed in any one of the preceding claims wherein the volume resistivity of the electrically conductive magnetic particles is 10^9 ohm.cm or less and the volume resistivity of the magnetic toner is 10^{12} ohm.cm or more.

11. A developer as claimed in any one of the preceding claims wherein the magnetic toner contains a charge control agent.

12. A developer as claimed in claim 8, wherein said charge control agent is Nigrosine, a monozao dye, zinc hexadecylsuccinate, an alkyl ester or alkyl amide of naphthoic acid, nitrohumic acid, N,N′-tetramethyldiminobenzophenone, N,N′-tetramethylbenzidine, triazine, or a metal complex of salicylic acid.

13. A developer as claimed in any one of the preceding claims further comprising a powdered material which can be triboelectrically charged to the same polarity as that of the latent electrostatic image to be developed, when said powder-like material is brought into contact with a development sleeve.

14. A developer as claimed in claim 9, wherein the powdered material is zinc oxide, titanium oxide, silicon oxide, magnesium oxide, aluminium oxide, aluminium oxide, calcium carbonate, magnesium carbonate, barium carbonate, barium sulphate, calcium sulphate, aluminium hydroxide, magnesium hydroxide, calcium silicate, magnesium silicate, clay, white carbon, alumina white or talc.

15. A developer as claimed in claim 13 or claim 14 containing from 0.1 to 5.0% by weight, based on the weight of the magnetic toner, of the powdered material.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon) Ltd.—1981.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.